# Environmentally Friendly Pretreatment for Department of Defense Applications

*SERDP Project WP-1676*

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# Report Documentation Page

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# SERDP-1676 Technical Objectives

- Develop an environmentally friendly pretreatment system for multi-material Department of Defense applications
  - Free of hexavalent chromium ($Cr^{6+}$)
  - No volatile hazardous air pollutants (HAPs)
  - Ease of application using existing infrastructure
  - Cost effective
  - **Broad substrate/topcoat compatibility**

# Current Zirconium Pretreatment Commercial Activity

- Over 60 general industrial lines converted to zirconium pretreatments (spray and immersion lines).

- Several major North American and European automotive OEM pretreatment lines converted to zirconium pretreatments

# Zirconium Pretreatment Benefits

**Performance**

- Excellent corrosion resistance
- Promotes coating adhesion to substrate

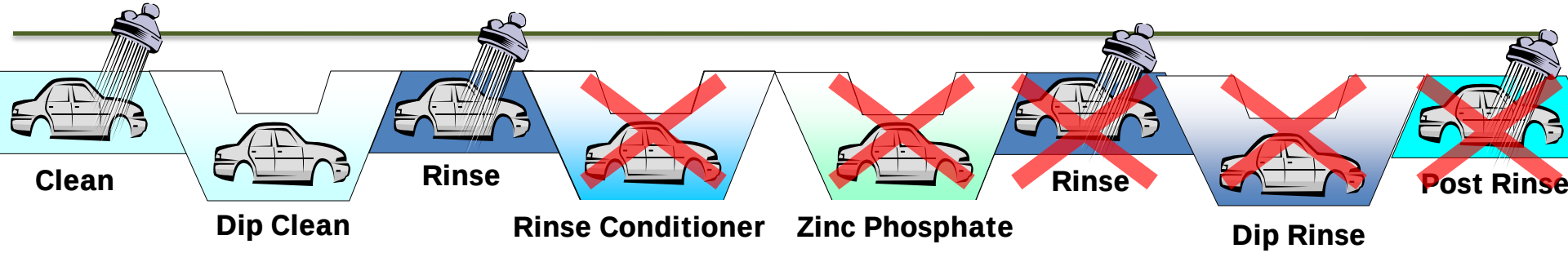
**Environmental**

- No volatile hazardous air pollutants (HAPs)
- Reduced waste concerns
  - 80% less waste than zinc phosphate
  - No regulated heavy metal species

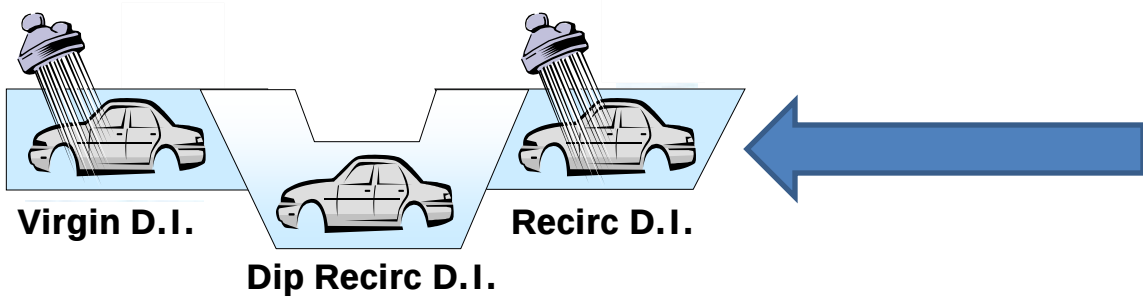
**Processing**

- Application at ambient temperature
- Milder pH than zinc phosphate and chromate pretreatments (pH = 4.5 vs. 1.5 – 3.0)

# Pretreatment Process

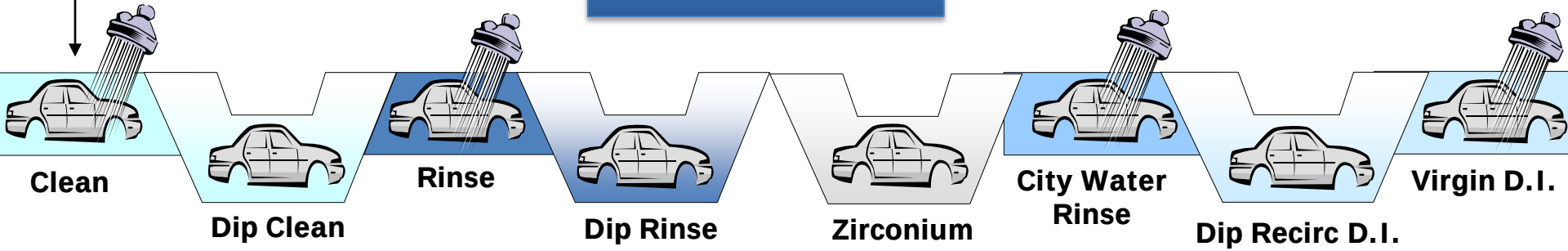



## Zn Phosphate Process




Deluge,
Pre-wipe

## Zirconium Process



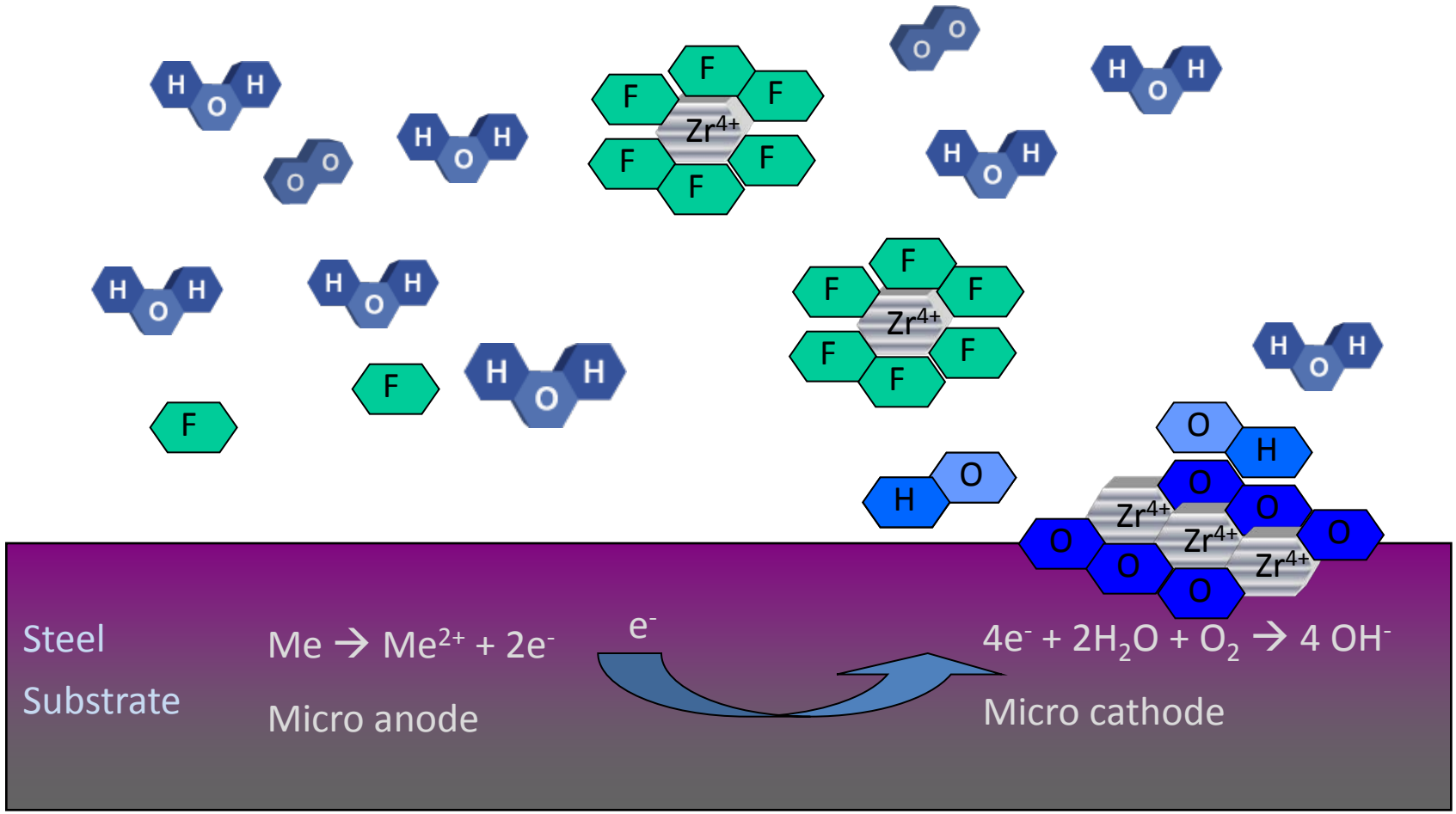
# Appearance of Zirconium Pretreatment

Before Zirconium Pretreatment

After Zirconium Pretreatment

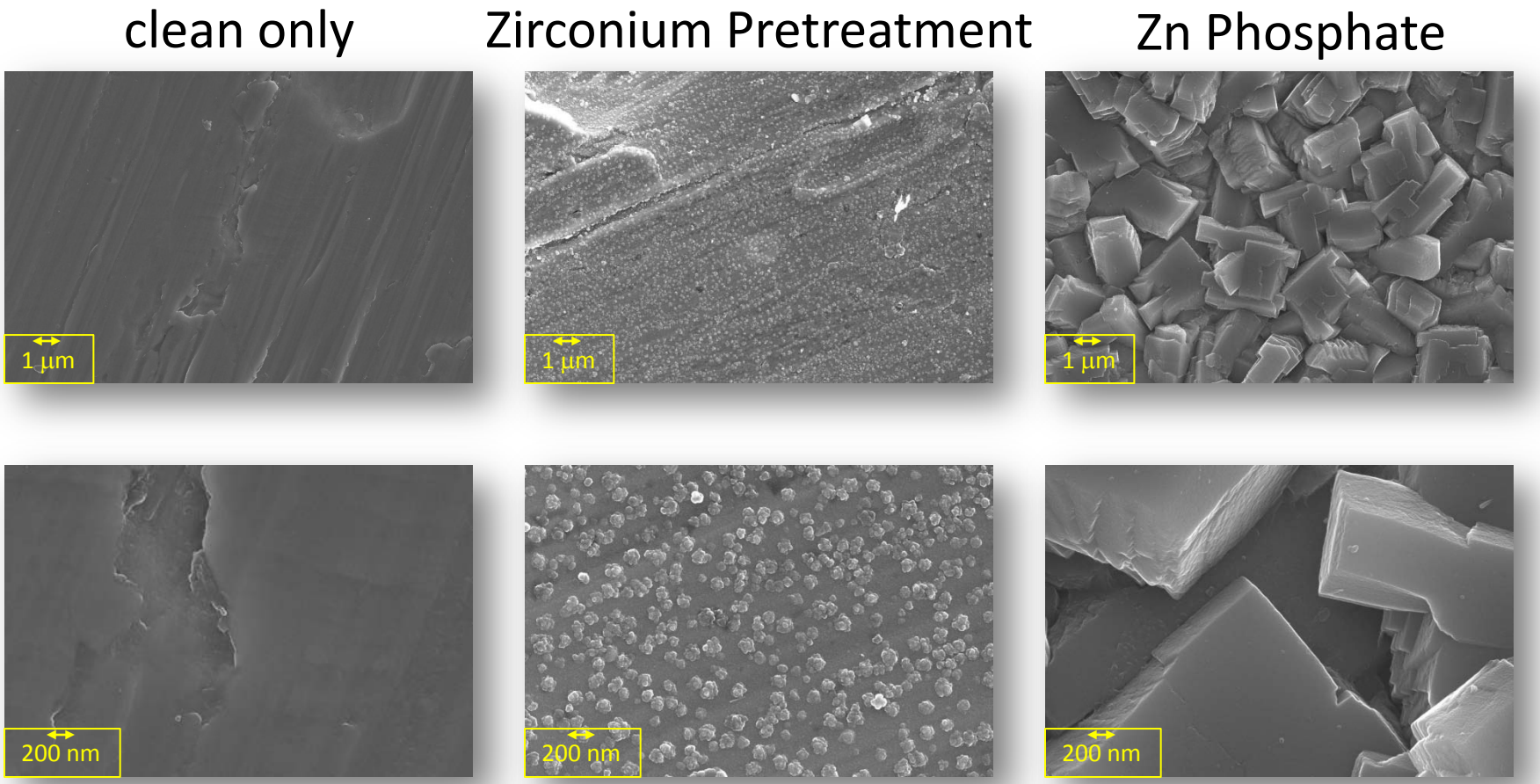
**Zirconium pretreatment coatings are visible.**

# Zirconium-Based Pretreatment




**Coating thickness: 20-200 nm.**

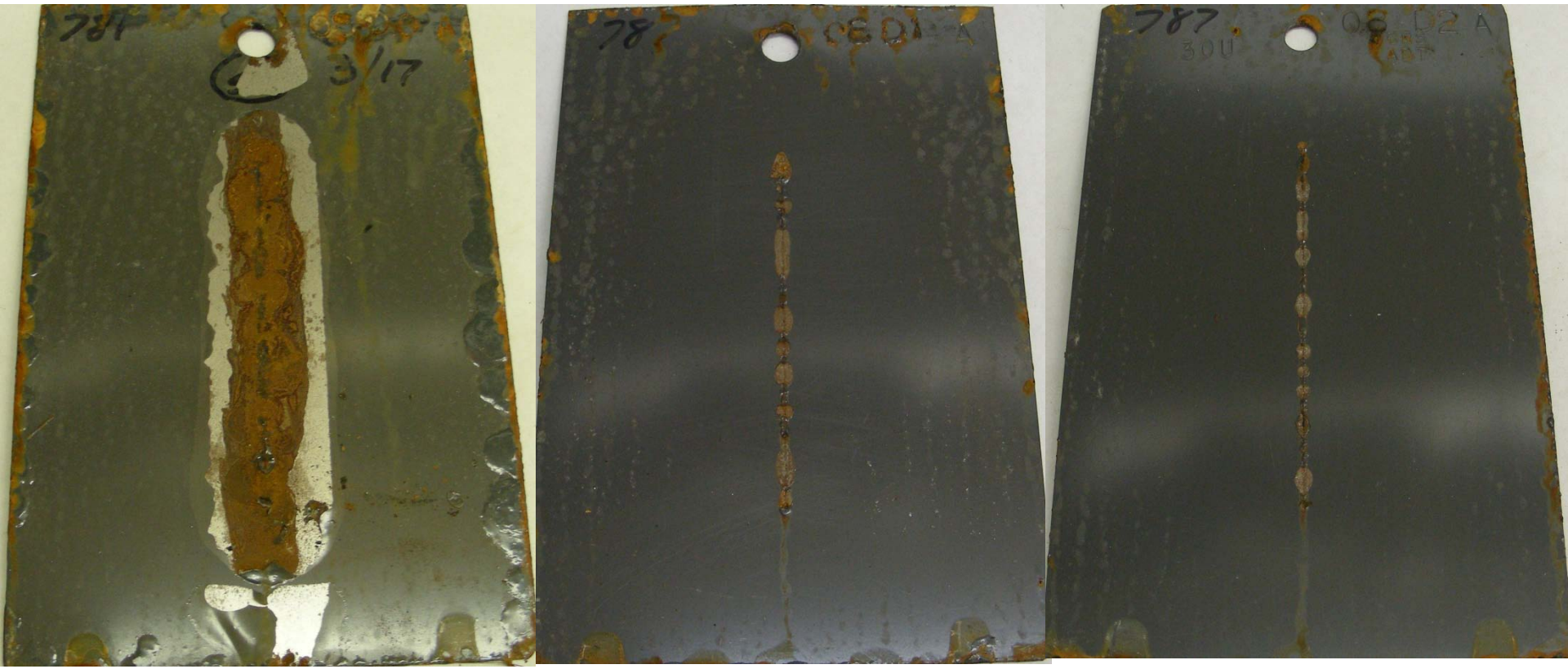
# Coatings on Cold-Rolled Steel




- Morphology and coating thickness of the zirconium pretreatments are unique when compared to zinc phosphate

# Commercial Pretreatment performance

cleaned only | Zirconium Pretreatment | Zinc phosphate



Modified GMW14872 with Electrocoat over CRS

# Environmentally Friendly Zirconium Oxide Pretreatment

**Task 1:** OEM Pretreatment Development

immersion-applied ZrOx

**Task 3:** Repair Pretreatment Development

**Task 2:** Depot Pretreatment Development

# Environmentally Friendly Zirconium Oxide Pretreatment

**Task 1:** OEM Pretreatment Development

immersion-applied ZrOx

- Evaluate commercial immersion formulae with DoD substrates and coatings - reformulate as needed (Mil-Spec testing at ARL).

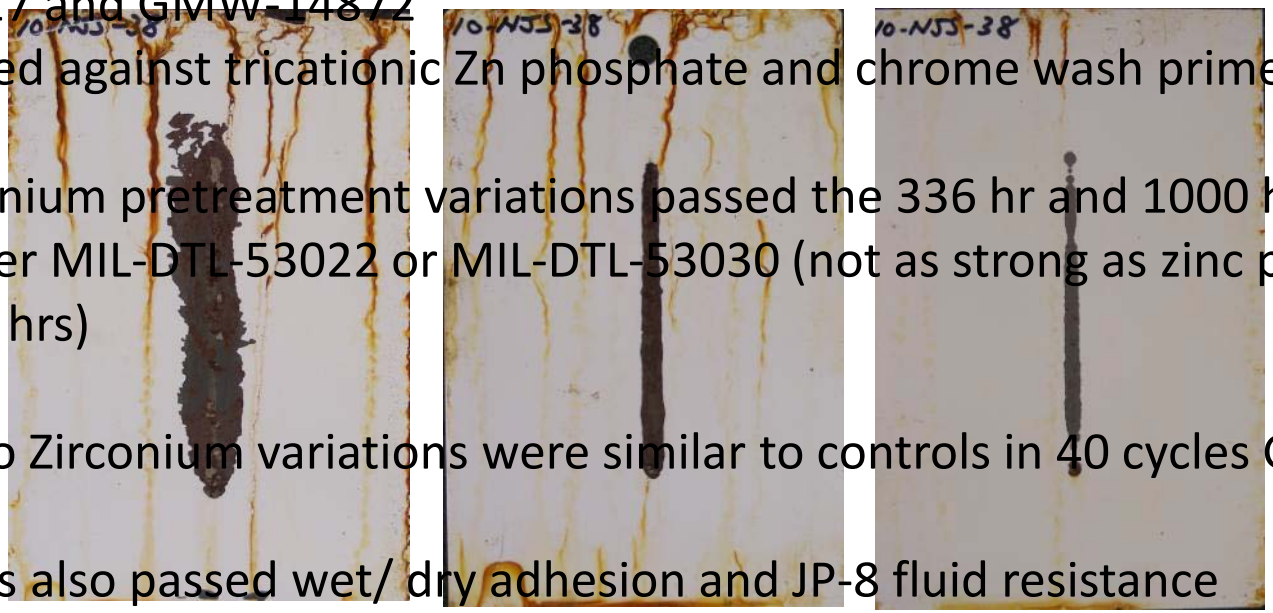
# Limited Mil-Spec testing at ARL: Immersion Pretreatment

- Samples submitted for accelerated corrosion testing (CRS, 2024-T3, and 7075-T6).
  - Commercial and experimental formula modifications submitted
  - B-117 and GMW-14872
  - Tested against tricationic Zn phosphate and chrome wash primer

- Two Zirconium pretreatment variations passed the 336 hr and 1000 hr B-117 outlined per MIL-DTL-53022 or MIL-DTL-53030 (not as strong as zinc phosphate after 1000 hrs)

- Same two Zirconium variations were similar to controls in 40 cycles GMW-14872

- Variations also passed wet/ dry adhesion and JP-8 fluid resistance



Commercial formula | Modified formula | Zn Phosphate

- Panels with passing results were sent to NASA's Cape Canaveral beachside corrosion site

500 hours B117 MIL-PRF-53022 Type II

# Environmentally Friendly Zirconium Oxide Pretreatment

- Visit DoD depot facilities to benchmark application process/conditions
- Determine compatibility of immersion formula with depot equipment.
- Formula optimization, if needed
- Comprehensive Mil-Spec testing

**Task 2:** Depot Pretreatment Development

# Benchmark of Depot Sites

Benchmark Depot Application Systems

**Marine Corps Logistics Base at Albany, GA**

- Uses immersion pretreatment
- Two tanks currently not in use suitable for zirconium pretreatment

**Letterkenny Army Depot**

- Uses immersion pretreatment
- Wash primer replacement high priority
- Would need to supply immersion tank for zirconium application

# Environmentally Friendly Zirconium Oxide Pretreatment

- Suitable for small areas
- Spray-Gun applied
- Wand applied
- Wipe-on

**Task 3:** Repair Pretreatment Development

# Field repair zirconium pretreatments

- Two potential formulations are in development:
  - Spray-on/ Rinse-off application
  - Dry-in-Place application

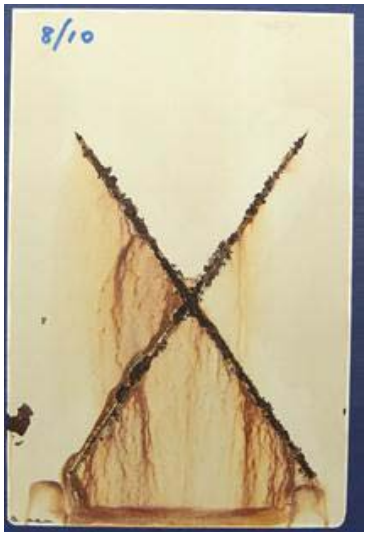
- Both materials utilize zirconium technology and are based on prototype formulations from Task 1
- Spray-on/ Rinse-off formula uses an inorganic shear-thinning rheology modifier
  - Material can be sprayed on using a hand or garden sprayer, but then "gels" after application; adheres to vertical surfaces until rinsed off
  - Need to collect rinse water

- Dry-in-place formula is designed to be spray applied, then ambient air dried

# Field repair zirconium pretreatments

- Limited Mil- spec testing by ARL:
  - Spray-on/ Rinse-off passed wet/dry adhesion and JP-8 testing
  - Dry-in-Place formulation had inconsistent wet adhesion
- Further development with application conditions of Dry-in-Place formula has resulted in a more consistent pretreatment coating

1000 hours B117 (MIL-DTL-53030 Type II)




Dry-in-Place


Zinc phosphate

# Path Forward

- Qualification to Mil specification
- Continue to develop a field application zirconium system appropriate for depot needs
- Proposal submitted to ESTCP for a demonstration/ validation of immersion technology at DoD depots

# Project Team SERDP WP-1676

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